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NMR spectra and relaxation in incommensurate systems in the presence of a devil's staircase

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Résumé. — La possibilité de faire la différence entre des phases vraiment incommensurables et des structures à longue période est discutée. Les résultats théoriques sont comparés avec ceux d'expériences effectuées sur Rb_2ZnCl_4, Rb_2ZnBr_4, et $[N(CH_3)_4]_2ZnCl_4$. Dans la plupart des cas, les effets dus à la présence d'un escalier du diable sont masqués par ceux des défauts.

Abstract. — The possibility of discriminating true incommensurate phases from long period commensurate phases *via* NMR lineshape and spin-lattice relaxation measurements is discussed. The theoretical results are compared with experimental data in Rb_2ZnCl_4, Rb_2ZnBr_4, and $[N(CH_3)_4]_2ZnCl_4$. Devil's staircase effects seem to be in the majority of cases masked by defects.

1. Introduction.

In incommensurate (I) systems the periodicity q_I of the order parameter $Q(x)$ and the periodicity q_p of the basic lattice cannot be expressed as a ratio of two integers :

$$q_I/q_p \neq M/N ; \quad M, N = 1, 2, 3, ... \qquad (1)$$

resulting in a loss of the translational symmetry of these systems. According to the Landau theory [1], which is based on the continuum approximation, the modulation wave vector q_I varies continuously with temperature.

It has been recently suggested [2, 3] that some of the incommensurate phases represent in fact a sequence of long period commensurate (C) phases where the superstructure wave vector varies in steps and « locks in » at an infinity of C values (i.e., it can assume values equal to all rational numbers). According to the « devil's staircase » model [2, 3] — which takes the discreteness of the crystal lattice explicitely into account — the phase diagram may consist of an infinity of C phases which may or may not be separated by an infinity of true I phases. The first of these two cases is known as the incomplete and the second as the complete devil's staircase [2, 3]. It may thus happen that a staircase type variation of the superstructure wave vector takes place in certain temperature intervals while elsewhere the superstructure wave vector may vary continuously so that a true I phase occurs. Long period C phases have been observed in thiourea [4] where there is a phase with a ninefold period and in $[N(CH_3)_4]_2ZnCl_4$ where there is a C phase with a period five times that of the high temperature phase [5]. A peculiar case is that of Rb_2ZnBr_4 where the modulation wave vector does not change at all for more than 140 K and equals 5/17, so that the unit cell should be 17 times that of the high T phase [6, 7]. This result is rather unusual since phases with a large superstructure should exist over a narrower range of temperatures than phases with a small superstructure. Close to the incommensurate — commensurate transition successive jumps in the wave vector were observed in this compound but the various « stairs » are not specified by an exact fraction and moreover seem to coexist in a certain temperature range [6, 7].

Experimentally it is rather hard to distinguish higher order C phases with large periods from true incommensurate phases [8]. Here we wish to show to what extent NMR can be used for this discrimination.

2. NMR spectra in I and higher order C phases.

Let us discuss the simplest possible case where the incommensurate shift of the NMR frequency linearly depends on the displacement of the nucleus so that we have in the I phase [9]

$$\nu(x) = \nu_0 + \nu_1 \cos \phi(x) . \tag{2}$$

Here ν_1 is proportional to the amplitude of the modulation wave ($\nu_1 \propto A$) and $\phi(x) = \mathbf{q}_c \mathbf{x}_\alpha + \phi_0 + \varphi(x)$ with $\mathbf{q}_c$ being a reciprocal lattice vector of the C phase, $\mathbf{x}_\alpha$ being a vector in the direct lattice designating the position of the nucleus in the unit cell, ϕ_0 being a phase shift and $\varphi(x)$ a solution of the Sine-Gordon equation which is generally incommensurate with the basic crystal lattice.

Equation (2) describes the spatial variation of the NMR frequency in the one-dimensionally modulated I phase. As one moves along the modulation direction, $\cos \phi(x)$ will nearly continuously take on all values between -1 and $+1$.

The NMR frequency distribution in the I phase is now obtained in the constant amplitude approximation [10] as

$$f(\nu) = \frac{\text{const.}}{\mathrm{d}\nu/\mathrm{d}x} = \frac{\text{const.}}{(\mathrm{d}\nu/\mathrm{d}\phi)(\mathrm{d}\phi/\mathrm{d}x)}, \tag{3}$$

yielding

$$f(\nu) = \frac{\text{const.}}{\sqrt{1 - \left(\frac{\nu - \nu_0}{\nu_1}\right)^2}\,(\mathrm{d}\phi/\mathrm{d}x)} . \tag{4}$$

In the plane wave limit, $\mathrm{d}\phi/\mathrm{d}x = \text{const.}$ and equation (4) yields a quasi-continuous frequency distribution limited by two edge singularities at $\nu - \nu_0 = \pm \nu_1$. The splitting between the edge singularities increases with decreasing temperature as $\Delta\nu = 2 \nu_1 \propto A \propto (T_I - T)^\beta$ where β is the critical exponent.

In a C phase $\varphi(x)$ becomes a constant, $\varphi(x) = K$, which just renormalizes the phase shift $\phi_0 \to \tilde{\phi}_0$. Expressing $\mathbf{q}_c$ in the presence of a devil's staircase as

$$\mathbf{q}_c = \mathbf{b}^x \frac{M}{N}, \tag{5}$$

where $\mathbf{b}^x$ is a reciprocal lattice vector of the high temperature phase and M, N are integers, expression (2) becomes

$$\nu^{(M,N)} = \nu_0 + \nu_1 \cos\left(2\pi \frac{M}{N} + \tilde{\phi}_0\right), \quad M = 0, 1, 2, ..., N-1 . \tag{6}$$

Expression (6) now yields the NMR frequencies in a commensurate unit cell which is N times larger than the high temperature unit cell.

The frequency distribution in a C phase with N non-equivalent sites per unit cell is a sum of delta functions

$$f(\nu) = \frac{1}{N} \sum_{M=0}^{N-1} \delta\left[\nu - \nu_0 - \nu_1 \cos\left(2\pi \frac{M}{N} + \tilde{\phi}_0\right)\right], \tag{7}$$

yielding N commensurate lines instead of the quasi-continuous incommensurate frequency distribution (4).

In the incommensurate phase the translational periodicity is lost and the whole crystal is a unit cell. The frequency distribution in the I phase is obtained from equation (7) in the limit that N becomes very large. In such a case the discrete distribution becomes continuous and we have to replace the sum in expression (7) by an integral

$$f(\nu) = \frac{1}{L} \int_{-\infty}^{+\infty} \delta[\nu - \nu(x)]\,\mathrm{d}x = \frac{1}{L}\frac{\mathrm{d}x}{\mathrm{d}\nu} . \tag{8}$$

The above result — which is obtained by introducing a new variable $u = \nu - \nu(x)$ so that $\mathrm{d}u = \frac{\mathrm{d}\nu}{\mathrm{d}x}\mathrm{d}x$ — is of course identical with equation (3). It is thus obvious that the NMR spectrum of a very long period C phase will eventually become practically identical with that of a genuine I phase. The question is when does this happen.

In evaluating the actual lineshape of the composite C spectrum we have to convolute $f(\nu)$ with the lineshape $L(\nu - \nu_c)$ of a single line :

$$F(\nu) = \int_{-\infty}^{+\infty} L(\nu - \nu_c)\, f(\nu_c)\,\mathrm{d}\nu_c . \tag{9}$$

If $L(\nu - \nu_c)$ is a Gaussian, the above integral can be evaluated explicitly and we obtain with the help of equation (7)

$$F(\nu - \nu_0) = \frac{1}{N} \sum_{M=0}^{N-1} \frac{1}{\sqrt{2\pi}\,\sigma} \times \exp\left\{-\left[\nu - \nu_0 - \nu_1\left(\cos 2\pi \frac{M}{N} + \tilde{\phi}_0\right)\right]^2 \Big/ (2\sigma^2)\right\}, \tag{10}$$

where $\sqrt{2}\,\sigma$ is the natural linewidth in the high temperature phase.

The splittings between the N commensurate lines will vary with N roughly as

$$\Delta\nu \approx \frac{2\nu_1}{N-1}, \tag{11}$$

where $2\nu_1$ is the total width of the spectrum. The C peaks will be smeared out and indistinguishable from an incommensurate plane wave type lineshape if

$$\sqrt{2}\sigma > \frac{2\nu_1}{N-1} . \tag{12}$$

Expression (12) thus yields the limits of NMR lineshape discrimination between I and higher order C phases. Various examples of computer generated higher order C spectra are shown in figure 1.

As an example let us consider the ^{14}N NMR spectrum of $[N(CH_3)_4]_2ZnCl_4$ where an incomplete devil's staircase has been reported to exist [5]. A given high temperature ^{14}N resonance line is replaced by an incommensurate frequency distribution $f(\nu)$ (Eq. (4)) in the I phase between $T_I = 23$ °C and $T_{c1} = 7$ °C. In the 5 c_0 C phase between $T_{c1} = 7$ °C and $T_{c2} = 3.5$ °C five C lines are found, as expected for the case that the unit cell is five times larger than the cell of the high temperature phase. In the second C phase below T_{c2}, where $c = 3\,c_0$, there are as expected only three C lines.

If the structure of the I phase would not be incommensurate but commensurate with a unit cell which is N times the paraelectric unit cell, then N must be significantly larger than 30. As can be seen from figure 2 the theoretical commensurate lineshape for $N = 30$ is still far from being close to the one experimentally observed at $T = 14$ °C since the C peaks would still clearly be discernible in contrast to what was observed. Here $\sqrt{2}\sigma$ is taken as 0.05 ν_1.

It thus seems that the « I » phase in $[N(CH_3)_4]_2ZnCl_4$ is a true incommensurate phase. If it would represent a sequence of higher order C phases (which would be on a T scale rather closely spaced) then the lowest order term of this sequence, N_L, corresponds to $N_L > 30$ instead of to $N_L = 7.9$ etc.

The situation is somewhat different in the high T part of the I phase in Rb_2ZnBr_4 where a « commensurate » value of the modulation wave vector 5/17 has been observed [6, 7]. The $1/2 \rightarrow -1/2$ ^{87}Rb NMR transitions are here significantly broader than in Rb_2ZnCl_4 and the resolution of the ^{87}Rb $1/2 \rightarrow -1/2$ NMR spectrum is not good enough [9] to discriminate between a true I phase and a phase with $N = 17$. The much higher resolution of the $1/2 \rightarrow 3/2$ ^{87}Rb satellite spectra [11] and the Br nuclear quadrupole resonance spectra [12] should however allow for a discrimination between an I phase and a C phase with $N = 17$. We thus believe that the observed behaviour [6, 7] close to the I-C transition is due to a large number of coexisting long period phases with different N values induced by defects rather than due to a devil's staircase.

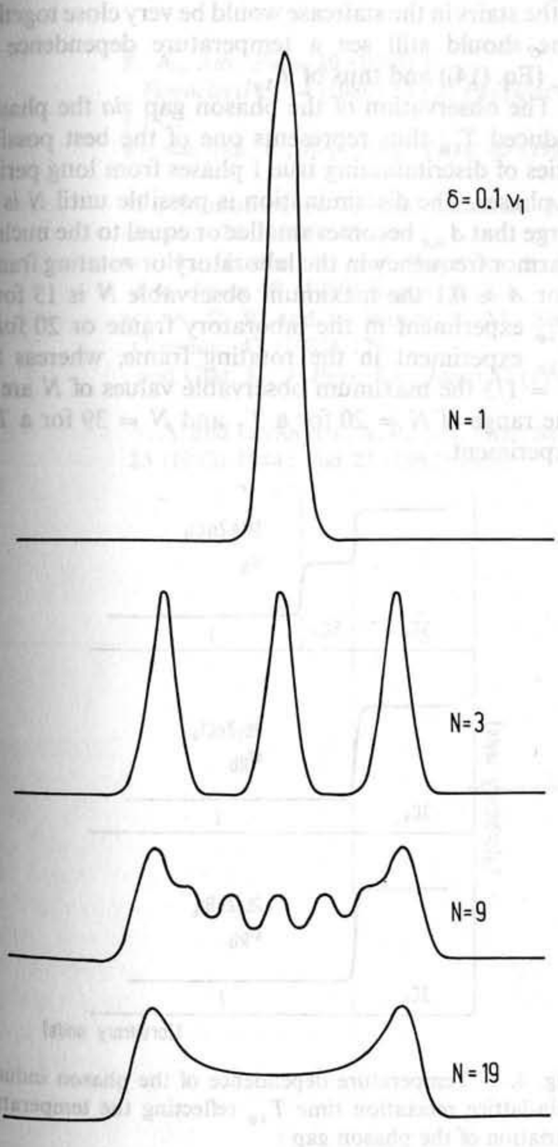

Fig. 1. — Computer generated NMR spectra in higher order C phases.

3. Temperature dependence of the spectra.

In the devil's staircase model the amplitude of the order parameter A varies continuously with temperature, whereas the wave vector locks in at all rational values (Fig. 3). The temperature dependence of the splitting between the two edge singularities in the I phase or the $\pm \nu_1$ lines in the devil's staircase C spectrum should be thus identical.

The formation of a multi-soliton lattice (where $d\phi/dx \neq$ const.) out of a plane wave modulation structure and the resulting appearance of C lines can be as well simulated in the devil's staircase model by a transition from longer to shorter period C phases.

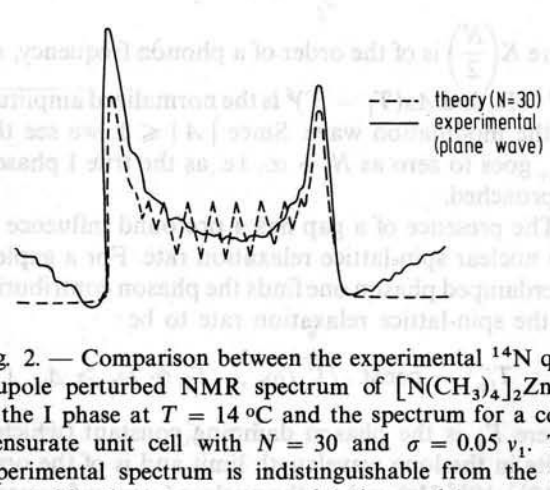

Fig. 2. — Comparison between the experimental ^{14}N quadrupole perturbed NMR spectrum of $[N(CH_3)_4]_2ZnCl_4$ in the I phase at $T = 14$ °C and the spectrum for a commensurate unit cell with $N = 30$ and $\sigma = 0.05\,\nu_1$. The experimental spectrum is indistinguishable from the one expected for the I plane wave modulation model.

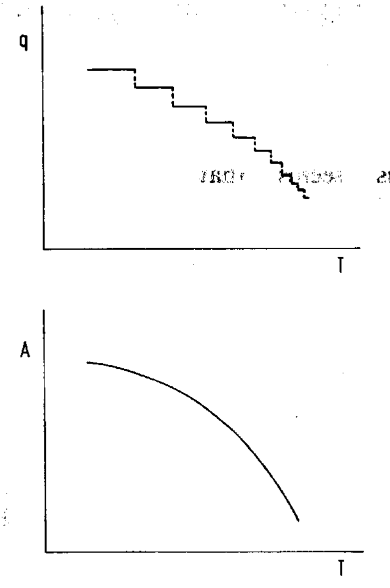

Fig. 3. — Schematic temperature dependence of the « lock-in » wave vector and the amplitude of the modulation wave in the case of a devil's staircase [2, 3].

In the devil's staircase model the modulation wave is pinned due to the discreteness of the crystal lattice. The observation of motional narrowing effects [10] in NMR is thus a sign that we are investigating a true I phase.

4. The phason gap and spin-lattice relaxation.

In a true I phase the phason spectrum

$$\omega_\varphi^2 = \Delta_\varphi^2 + \kappa^2 k^2, \quad \bar{k} = \bar{q} - \bar{q}_1 \tag{13}$$

is gapless (i.e. $\Delta_\varphi \equiv 0$). In a long period commensurate phase with a unit cell which is $N/2$ that of the high temperature phase, there still is a phason-like mode but the gap Δ_φ is non-zero [8] :

$$\Delta_{\varphi,c}^2 = K^2\left(\frac{N}{2}\right)^2 A^{N-2}. \tag{14}$$

Here $K\left(\frac{N}{2}\right)$ is of the order of a phonon frequency, say 10^{13} Hz, and $A \alpha (T_1 - T)^\beta$ is the normalized amplitude of the modulation wave. Since $|A| \leqslant 1$, we see that $\Delta_{\varphi,c}$ goes to zero as $N \to \infty$, i.e. as the true I phase is approached.

The presence of a gap has a profound influence on the nuclear spin-lattice relaxation rate. For a gapless, overdamped phason one finds the phason contribution to the spin-lattice relaxation rate to be

$$T_{1\varphi}^{-1} = \text{const.} \sqrt{\Gamma_\varphi / \omega_L}, \quad \Gamma_\varphi \gg \omega_L \geqslant \Delta_\varphi \tag{15}$$

where Γ_φ is the phason damping constant (which is finite in the long wavelength limit and is of the order of 10^{11}-10^{12} Hz) and ω_L the nuclear Larmor frequency either in the laboratory frame, $\omega_L = 10^7 - 10^8$ Hz, or in the rotating frame, $\omega_L = \omega_1 \sim 10^5$ Hz.

In the opposite case of a large phason gap one finds :

$$T_1^{-1} = \text{const.}\ \Gamma_\varphi/\Delta_\varphi, \quad \Delta_\varphi \gg \omega_L, \sqrt{\Gamma_\varphi \Delta_\varphi}. \tag{16}$$

A gapless phason thus yields a large, temperature independent, but Larmor frequency-dependent, spin-lattice relaxation rate. In the presence of a gap $\Delta_\varphi \gg \omega_L$ the phason induced spin-lattice contribution is much smaller and frequency independent. Moreover $T_{1\varphi}$ is directly proportional to the gap, Δ_φ (Fig. 4). In the presence of a devil's staircase, where equation (14) for Δ_φ applies, one should thus see jumps in $T_{1\varphi}$ (due to jumps in Δ_φ) as one moves from one C phase to another along the staircase. Such jumps in $T_{1\varphi}$ have been indeed observed [13] at the $5\,c_0 \to 3\,c_0$ transition in $[N(CH_3)_4]_2ZnCl_4$ and at the I-C transitions [9] in Rb_2ZnCl_4 and Rb_2ZnBr_4 (Fig. 4).

No such jumps were however observed within the I phase in contrast to the devil's staircase model. Even if the stairs in the staircase would be very close together one should still see a temperature dependence of Δ_φ (Eq. (14)) and thus of $T_{1\varphi}$.

The observation of the phason gap *via* the phason induced $T_{1\varphi}$ thus represents one of the best possibilities of discriminating true I phases from long period C phases. The discrimination is possible until N is so large that $\Delta_{\varphi,c}$ becomes smaller or equal to the nuclear Larmor frequency in the laboratory or rotating frame. For $A \approx 0.1$ the maximum observable N is 13 for a $T_{1\varphi}$ experiment in the laboratory frame or 20 for a $T_{1\rho}$ experiment in the rotating frame, whereas for $A = 1/3$ the maximum observable values of N are in the range of $N = 20$ for a T_1 and $N = 39$ for a $T_{1\rho}$ experiment.

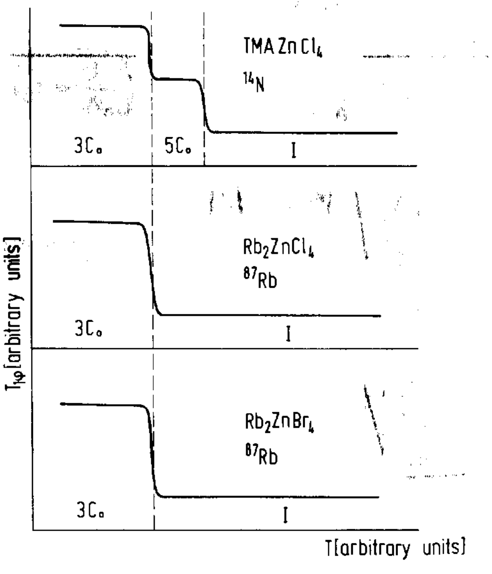

Fig. 4. — Temperature dependence of the phason induced spin-lattice relaxation time $T_{1\varphi}$ reflecting the temperature variation of the phason gap : a) ^{14}N $T_{1\varphi}$ in $[N(CH_3)_4]_2ZnCl_4$; b) Rb $T_{1\varphi}$ in Rb_2ZnCl_4; c) Rb $T_{1\varphi}$ in Rb_2ZnBr_4.

The above method is applicable to an ideal defect-free crystal. Impurities will pin the modulation wave and produce a defect induced gap Δ_i, which will be however in contrast to Δ_c nearly T-independent.

The observation of a sizeable phason gap in the plane wave modulation part of the I phase [13, 9] where commensurability effects are negligible demonstrates that the phason gap in the I phase — but not in the 5 c_0 and 3 c_0 phases — is induced by random frozen defects [13-15]. Such random frozen defects have been shown [14] to destroy the true long range order in I systems where the order parameter has continuous symmetry. Our results thus imply that, for systems discussed in this paper, true long range order is destroyed so that these systems are incommensurate only on the average and in fact consist of randomly pinned domains.

These domains — which exist already in the plane-wave modulation part of the I phase — must be rather large since anomalous broadening of the incommensurate X-ray satellites has been observed only close to the I-C transition T_c. The domains of course exist also in the multisoliton lattice modulation regime close to T_c. Their presence would prevent the observation of changes in the NMR line-shape and phason gap produced by the possible existence of higher order C phases stable over a narrow range of temperatures as predicted by the devil's staircase model [2, 3]. Only low order C phases (where the multiplication of the high temperature unit cell is relatively small and the temperature range of stability relatively large) produce large enough changes in the NMR spectrum and phason gap to be observable [13]. Devil's staircase effects thus seem to be in the majority of cases masked by defects.

References

[1] COWLEY, R. A., *Adv. Phys.* **29** (1980) 1.

[2] AUBRY, S., *Ferroelectrics* **24** (1980) 53 ; *J. Physique* **44** (1983) 147.

[3] For a review see BAK, P., *Rep. Prog. Phys.* **45** (1982) 587.

[4] DENOYER, F., MOUDDEN, A. H. and LAMBERT, M., *Ferroelectrics* **24** (1980) 43.

[5] MASHIYAMA, H., HASEBE, K. and TANISAKI, S., *J. Phys. Soc. Japan* **49** (1980) Suppl. B, 92.

[6] HOGERVORST, A. C. R. and DE WOLFF, P. M., *Solid State Commun.* **43** (1982) 179.

[7] IZUMI, M. and GESI, K., *J. Phys. Soc. Japan* **52** (1983) 2526.

[8] GOLOVKO, V. A. and LEVANYUK, A. P., *Sov. Phys. Solid State* **23** (1982) 1844 ; *ibid* **23** (1982) 1850.

[9] For a review see BLINC, R., *Phys. Reports* **79** (1981) 331, and references theorein.

[10] BLINC, R., PRELOVŠEK, P. and KIND, R., *Phys. Rev.* **B 27** (1983) 5404.

[11] SCHNEIDER, E. and PETERSSON, J., *J. Phys.* **B 46** (1982) 169.

[12] BELOBROVA, J. A., ALEKSANDROVA, I. P. and MOSKALEV, A. K., *Phys. Status Solidi (a)* **68** (1981) K17.

[13] BLINC, R., AILION, D. C., DOLINŠEK, J. and ŽUMER, S., *Phys. Rev. Lett.* **54** (1985) 79.

[14] IMRY, Y. and MA, S., *Phys. Rev. Lett.* **35** (1975) 1399.

[15] LEDERER, P., MONTAMBAUX, G., JAMET, J. P. and CHAUVIN, M., *J. Physique Lett.* **45** (1984) L-627. See also UNRUH, H. G., *J. Phys. C* **14** (1983) 3245.